



The
Patent
Office

PCT/GB 00/00753
09/914920

| | | |
|-------|--------------------------|-----------|
| REC'D | 20 MAR 2000 | IN PEOPLE |
| WIPO | PCT The Patent Office | |

Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ



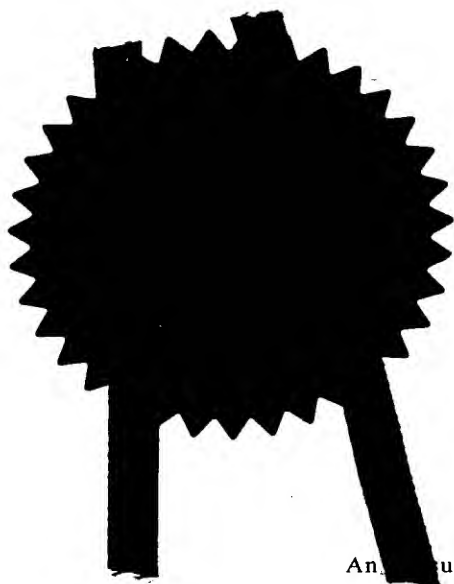
**PRIORITY
DOCUMENT**
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

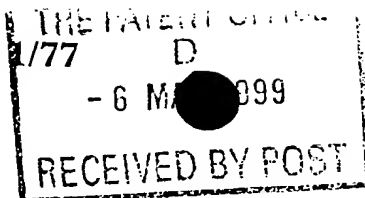
Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed

Dated

11 FEB 2000



The
Patent
Office

08MAR99 E430497-4 D02806
P01/7700 0.00 - 9905098.1

1/77

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet, from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

1. Your reference JL2022/DERA/P2816

2. Patent application number
(The Patent Office will fill in this part) **9905098.1**

3. Full name, address and postcode of the or of each applicant (underline all surnames)
THE SECRETARY OF STATE FOR DEFENCE
DEFENCE EVALUATION AND RESEARCH AGENCY
FARNBOROUGH
HANTS
GU14 OLX

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

UNITED KINGDOM

54510003

4. Title of the invention IMPROVEMENTS RELATING TO ANNEALING

5. Name of your agent (if you have one) Barker Brettell

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

138 Hagley Road
Edgbaston
Birmingham
B16 9PW

Patents ADP number (if you know it)

7442494002 ✓

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

| Country | Priority application number (if you know it) | Date of Filing (day/month/year) |
|---------|--|---------------------------------|
|---------|--|---------------------------------|

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

| Number of earlier application | Date of filing (day/month/year) |
|-------------------------------|---------------------------------|
|-------------------------------|---------------------------------|

8. Is a statement of inventorship and of right to grant of a patent required in support of this request (Answer 'Yes' if:
a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

YES

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form -

Description 24 x 24

Claim(s) 9 x 9

Abstract 1 x 1

Drawing(s) 6 x 6

10. If you are also filing any of the following, state how many against each item.

Priority documents -

Translations of priority documents -

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*) 1

Request for preliminary examination (*Patents Form 9/77*) 1

Request for substantive examination (*Patents Form 10/77*)

Any other documents
(please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature

Date

Barker Brettell

05/03/1999

Name and daytime telephone number of person to contact in the United Kingdom

JOHN LAWRENCE

Tel: 0121 456 1364

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 01645 500505
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

IMPROVEMENTS RELATING TO ANNEALING

This invention relates to improvements in annealing, and in particular to a method and apparatus for annealing ferroelectric thin film materials.

5

There has been a considerable amount of research into the development of devices which utilise the thermal properties of ferroelectric materials. One example is the development of infrared imaging cameras based on two-dimensional arrays of ferroelectric thermal detectors which are attractive due to their near ambient temperature operation. Thermal detectors used for infra-red imaging rely on the temperature change of the sensing material due to absorption of infra-red radiation. With ferroelectric materials this radiation causes a change in the electrical polarisation of the material which enables the magnitude of the change in temperature to be detected.

10
15

In order to reduce the size of the detectors, combined integrated ferroelectric devices have been developed in which the ferroelectric material is combined with the electronic read out circuitry in a single device. Typically, these devices comprise layered structures with a thin layer of ferroelectric sputtered or spin coated or otherwise deposited onto or above one or more base layers. Other examples of such integrated ferroelectric devices are thin film piezoelectric actuators and ferroelectric random access memories (FeRAM).

20
25

The combination of the ferroelectric material with the active circuitry in one package produces a more compact device than the provision of a separate read out circuit and improves yield, reduces cost and improves performance. However, a fundamental problem with such devices is the need to deposit the ferroelectric material within a thermal budget that is

30

compatible with the integrated circuitry not being damaged or destroyed by elevated temperatures. It is widely recognised that exposure of an integrated circuit to temperatures above 450°C is a constraint on the processing of chips/materials with IC content, and this conflicts with the growth requirements of many ferroelectric layers.

A particularly important family of ferroelectric materials in use and under investigation for IR detector, actuator or FeRAM applications is the perovskites. This family include materials such as lead scandium tantalate (PST), lead zirconate titanate (PZT), barium strontium titanate (BST), lead titanate (PT) and others. For use as a ferroelectric the material layer must be in the perovskite phase. It can either be deposited directly into that phase at an elevated temperature or at a lower temperature which is then subsequently annealed into the ferroelectric perovskite phase. Layers deposited at low temperatures are generally in an amorphous, pyrochlore or other phase which is incapable of exhibiting ferroelectricity. For PST, for example, the material must be deposited at temperatures in excess of 450°C to enter the perovskite phase. Direct depositing of these materials in a perovskite phase is therefore incompatible with the temperature budgets of integrated circuitry.

One known way of providing a layer of ferroelectric material in the perovskite phase without damaging an ROIC provided on a base layer is to deposit the material in a non-ferroelectric state at a low temperature (say less than 450°C). The material may then be annealed using a laser to heat the layer sufficiently to convert the material into its perovskite phase.

In order to understand the effect of laser annealing, consider the structure of a typical uncooled microbridge type IR detector. From the top surface downwards prior to the electrode deposition, the layers of material are as

given in Table 1.

| Material | Thickness | Purpose |
|------------------|---------------|---------------------------|
| PST | 1 μ m | Ferroelectric |
| Pt | 1000Å | Bottom electrode |
| Ti | 50Å | Adhesion layer |
| SiO ₂ | 1000Å | Barrier layer |
| Sac | 1-2.5 μ m | Sacrificial layer |
| SiO ₂ | 0.8 μ m | Passivation/barrier layer |
| ROIC | | Active circuitry |
| Si | 500 μ m | Substrate wafer |

Table 1

5

In order to heat the PST layer sufficiently without damaging the ROIC (Read Out Integrated Circuitry) layer, the laser wavelength must be chosen so that strong absorption occurs in the PST layer. The temporal width of the pulse must also be kept sufficiently short that the heat diffusion length is small enough to prevent the induced heat wave from penetrating through the layers to the ROIC layer. For relatively thin layers up to, say, 1000Å these criteria are satisfied by commercially available excimer lasers. These lasers operate in the ultraviolet (UV) and have short pulse lengths of around 25ns. Pulses are delivered to the layer as either a single shot or at a slow repetition rate of 100's of Hz or thereabouts. The measured reflectivity of low temperature deposited (non-perovskite) PST at the wavelength of a typical commercial excimer laser of 248nm is 21%. This indicates strong absorption, whilst the absorption length at this wavelength, calculated from experimental data, is 19nm indicating strong surface absorption.

20

To generate sufficient temperature at the bottom of a thick layer of PST (greater than 1000Å) requires relatively high energy density excimer lasers. Increasing the power increases the surface temperature. This
5 places a limit on the maximum possible thickness of PST which can be annealed at around 1000Å due to extreme surface heating which can cause surface damage, poor crystallisation and crystal quality, poor film physical integrity and loss of stoichiometry due to evaporation of volatile components. As a result, the use of such a laser is unsatisfactory for
10 layers above, say 2000Å (and more so for even thicker layers), with extremely high temperatures being generated at the surface of the layer and high thermal gradients being generated in the PST due to the short absorption and diffusion lengths resulting from the short pulse duration.

15 An object of the present invention is to overcome or alleviate the problems involved in the laser annealing of relatively thick layers of ferroelectric materials posed by the constraints of commercially available lasers.

20 In accordance with a first aspect, the invention provides a method of producing an integrated ferroelectric device comprising a first layer of material capable of existing in a ferroelectric state and a second layer of material defining an integrated circuit, the method comprising the steps of:
of:

25

producing a pulse of energy having a first temporal width;

extending the temporal width of said pulse by passing it through a temporal extender to produce a processed pulse having a greater temporal

30

width; and

illuminating the first layer with said processed pulse to convert some or all of the material in the first layer from a non-ferroelectric state into a phase capable of exhibiting ferroelectricity or otherwise improving the quality of the material of the first layer without exceeding the temperature budget of the integrated circuit of said second layer.

The method may further comprise generating a number of such processed pulses and sequentially illuminating the device with said pulses.

10

Preferably, the material of the first layer comprises a low grade deposited perovskite and the method improves the quality (i.e. greater crystal order and/or crystal size) of the perovskite material. Alternatively, the material may be deposited substantially in a non-perovskite phase and the method converts some or all of the material into the perovskite phase.

15

Preferably, the pulse of energy comprises a pulse of energy produced using a laser. More than one such pulse may be produced, with each pulse being temporally extended. The first layer may be sequentially illuminated by a number of such processed pulses.

20

By providing a temporal extender, it is possible to deliver the laser energy to the first layer at a slower rate than is possible with a non-extended laser pulse using commercially available laser sources. This increases the diffusion length in the material ensuring more even heating throughout the layer and reduced surface temperatures at the face of the first layer nearest the laser source.

25

The laser pulse may be produced using an excimer laser. It may have a wavelength in the ultraviolet of around 248nm (for a KrF excimer laser).

30

Alternatively, the pulse may be produced using a CO₂ laser.

The pulse produced by the laser may have a temporal length of substantially 10ns, or 20ns or perhaps substantially 25ns, or even beyond
5 or any value within a range of values limited by one or more of the preceding values. This represents the limit for current commercially available excimer lasers.

The temporal extender may increase the temporal length of the pulse to
10 produce a processed pulse with a temporal length of approximately 300ns, or between substantially 300ns and 400ns, or perhaps longer. For instance, the processed pulse may have a temporal length that is an order of magnitude greater than the unprocessed pulse.

15 The extended pulse may comprise more than one sub-pulse, each sub-pulse corresponding to a pulse action of the extender. These may be separated by a known time interval to produce a sequence of closely spaced sub-pulses defining the processed pulse. The temporal width of each subpulse may correspond to the temporal width of the unprocessed
20 pulse. They may be separated by, say, substantially 25ns or substantially 30ns or substantially 50ns or less or more or any range bounded by one of the values. In the case of ten sub pulses, an processed pulse with a temporal width of about 400ns is produced.

25 The processed pulse may, therefore, comprise two, three, four, or perhaps ten or more sub-pulses which are temporally spaced close together to form a processed pulse. By close we mean that the spacing between sub-pulses may be less than the width of each sub-pulse or perhaps equal to the sub-pulse width, or larger than the sub pulse width.

Each sub-pulse may be produced by partial reflection of the unprocessed pulse within the temporal extender.

5 The method may comprise producing a processed pulse having a fluence and temporal width that is compatible with the properties of the material of the first layer such that the temperature throughout the layer (or over a substantial depth of the first layer) exceeds a predetermined anneal temperature whilst the temperature of the second layer is within the temperature budget of the circuitry.

10

In one especially useful embodiment, the processed pulse properties (including fluence, temporal width and wavelength) may be selected so that the whole of the first layer exceeds the transition temperature for placing the material into a ferroelectric perovskite phase. This may be
15 greater than 450°C. At the same time, the peak temperature in the second layer may be kept lower than 450°C.

The first layer may comprise a layer of PST (or other material) of thickness of substantially 0.1µm, or perhaps substantially 1µm, or
20 perhaps substantially 0.8µm or substantially 1.2µm or any value therebetween.

The first layer may comprise the top layer of the device. Alternatively, it may have other layers provided both above and below it defining a
25 sandwich like structure. The integrated circuitry may be provided below the first layer.

In a refinement of the method, at least one additional layer may be provided above the first layer (i.e. on the opposite side to the second
30 layer).

Two different sources of energy may be used, each source producing a respective pulse and each respective pulse being extended by a pulse extender to produce a processed pulse. The first layer may then be
5 illuminated by both processed pulses. This may be either substantially simultaneously or sequentially.

The different sources of energy may comprise two different lasers, each generating a pulse of a different wavelength. For instance, one source
10 may comprise a KrF laser or other type of excimer laser, whilst the other source comprises a carbon dioxide (CO₂) laser.

In one arrangement, the method may include providing a metallic layer between the first layer and the second layer and illuminating the first
15 layer with two different processed pulses. A CO₂ laser and a KrF laser may be used whereby two effects arise. Firstly, the first layer is heated from the top down by the KrF laser pulse. Secondly, the first layer is heated up from the bottom upwards due to heating of the metallic layer when excited by the CO₂ laser pulse. This effectively heats the layer
20 from both sides.

The fluence of the pulse may be substantially be 0.05 J/cm², 0.1J/cm², 0.2J/cm² or perhaps a higher value or a lower value. It may be selected to be any value within a range bounded at its upper limit and/or lower
25 limit by one or more of these values. For example, it may be in the range 0.05-0.1J/cm² or 0.1-0.2J/cm² or 0.05-0.1J/cm².

The temporal width and fluence of the processed pulse may also be chosen to match the thickness, and properties of the first layer materials so that
30 the surface temperature at the first layer (i.e. the surface exposed to

radiation) does not exceed a predetermined maximum temperature. Using a suitable processed pulse width on a $1\mu\text{m}$ layer, it is possible to keep the surface temperature below the perovskite melting temperature of approximately 1500°C (depending on the material used).

5

Of course, it will be readily appreciated that instead of commencing with a short pulse having a first temporal duration, and extending the pulse, a longer initial pulse could be employed by using a bespoke laser device. However, this would prove more costly and so is not preferred. We may wish to seek protection for such a method in which a non-extended pulse is used.

10

In a refinement, the first layer may be illuminated with the processed pulse whilst the ambient temperature of the device is maintained higher than room temperature. An ambient temperature in the range 100°C - 450°C , or 200°C - 450°C , or any other range between the limits 100°C and 500°C approximately could be used. An ambient temperature of 300°C is preferred. This means that it is possible to use a lower energy laser pulse source it has less work to do to raise the temperatures above the phase transition temperature. In a further refinement, the laser light could illuminate the substrate during deposition of the first layer.

15

20

It will also be appreciated that there may be a considerable time delay between depositing the layer (or layers) forming the device and the annealing steps. For instance, the device layers may be deposited in one factory or room within a factory before moving to another room or factory to be annealed. Indeed, the method may find application in annealing any device having first and second layers at any time in its life or before or after use.

25

30

The first layer of material may be deposited at a temperature below that needed to form perovskite and may be deposited substantially wholly as non-perovskite phase. For instance, for PST a non-perovskite layer would be produced by depositing at below 300°C (to produce an amorphous material) or between 300°C or at 500°C to produce a pyrochlore material. The higher the temperature used to deposit, the more likely that some of the material will exist in the perovskite phase before annealing. Of course, the temperature used to deposit the material must not exceed the temperature budget of the second layer.

10

By temperature budget, the skilled man will of course appreciate that we mean the maximum temperature that the second layer can be heated to without causing unacceptable damage or degradation to the second layer.

15 In accordance with a second aspect, the invention provides an apparatus for producing an integrated ferroelectric device, said device comprising at least a first layer of material capable of existing in a perovskite phase and second layer of material defining an integrated circuit, the apparatus comprising:

20

pulse generating means adapted to generate a pulse of energy having a first temporal width;

pulse extending means adapted to extend the temporal pulse width of said pulse to provide a processed pulse of greater temporal width;

25

and guide means adapted to guide said processed pulse of energy onto said first layer whereby some or all of the material in the first layer is converted from a non-ferroelectric state into a ferroelectric state or to otherwise improve the quality of the material of the first layer without

30

exceeding the temperature budget of the integrated circuit of said second layer.

5 The apparatus may further comprise depositing means for depositing said first layer of material above said second layer in which some or all of said first layer is in a non-perovskite phase.

10 The pulse generating means may, for example, comprise a laser such as an excimer laser, such as a krypton fluoride (KrF) laser. Alternatively, it may comprise a carbon dioxide (CO₂) laser. The laser may have a wavelength in the ultraviolet spectrum, for instance 248nm. An example of a suitable laser is the Lambda Physik LPX210i Krf excimer laser.

15 The depositing means may be adapted to deposit a first layer of material above the second layer after one or more intermediate layers are deposited onto the second layer. One of these intermediate layers may comprise a sacrificial layer that is subsequently removed to leave a space between the first and second layers to form a microbridge. By providing electrical contacts between the integrated circuitry of the second layer and the first
20 layer the device may act as an infrared thermal detector.

Removal means may therefore be provided for removing the sacrificial layer. The layer be removed before or after the first layer is annealed.

25 The device may comprise a thermal detector such as a pyroelectric or dielectric bolometer type infrared detector. This may comprise an array of device defining a thermal imaging camera, perhaps an uncooled array. Alternatively, it may comprise a piezoelectric actuator or perhaps a ferroelectric random access memory. A number of devices may be
30 provided in an array on a single wafer. Of course, in a modification it

will be within the scope of protection sought to provide an apparatus for annealing any device which includes a first layer that is to be annealed (perhaps not ferroelectric) and a second layer which is sensitive to overheating.

5

Where an array of devices are provided, the processed pulse may illuminate more than one or preferably all of the devices in the array simultaneously. Alternatively, the processed pulse may be applied sequentially to the devices by scanning a laser beam made up of a number of processed pulses across the array of devices. In another arrangement, the laser may be fixed whilst the array of devices moves relative to the laser using one or more translation stages.

The apparatus may further include means for raising the ambient temperature of the integrated device during annealing. This may comprise a heating element upon which the device is placed.

The apparatus may further comprise means for evacuating the air from around the device during annealing. For example, a vacuum chamber may be provided with the device being placed in the vacuum chamber. An inlet port may be provided whereby the chamber can be filled with one or more gases, such as oxygen, during the annealing.

The pulse extender may be adapted to increase the temporal pulse width of the first pulse by substantially two times or four times, or substantially ten times or more than ten times or any value therebetween. In one arrangement, the pulse extender may be adapted to produce a processed pulse that comprises a number of sub-pulses, each sub pulse corresponding to the first pulse. This may be achieved using partial multiple reflections of the first pulse. A suitable pulse extender can be

obtained from Exitech Limited, Hanborough Park, Long Hanborough, Oxford, OX8 8LH.

5 In accordance with a third aspect, the invention provides an integrated ferroelectric device comprising at least a first layer of ferroelectric material and a second layer comprising an integrated circuit, in which said first layer is transformed into a perovskite phase using a pulse of energy from a laser that has been temporally extended.

10 The first layer may comprise a material selected from the class of material which can exist in a perovskite phase, such as PST, lead zirconate titanate (PZT), barium strontium titanate (BST), lead titanate (PT) and others.

15 The second layer may comprise silicon, silicon oxide and the requisite metallisation and implant doping layers to define the integrated circuit. Of course, other materials are possible.

20 The device may comprise a microbridge. This may form a part of an imaging device to detect incident radiation. An array of devices may be provided, for example to produce a two-dimensional image of a scene. In this case, the first layer may be spaced from the second layer to define a bridge overlapping the second layer.

25 The upper surface of the bridge may have a metal coating. The lower surface of the bridge may have a metal coating as well as or instead of the upper layer. The metal coating on the lower surface of the bridge may comprise a platinum layer overlapping a titanium layer. The metal coating on the upper surface may comprise a titanium layer.

30 The integrated circuit of the second layer may comprise a read out

integrated circuit (ROIC). It may include an amplifier adapted to amplify signals from the first layer.

5 A barrier layer, such as silicon dioxide may be provided on the lower surface of the bridge. This may overlap any metallic layer that is present. The second layer may also be provided with a barrier layer. Again, this may be silicon dioxide for example. The barrier layers prevent sacrificial material which defines the gap between the first and second layers from reacting with the layers during manufacture of the device. Of course, in
10 the finished device, substantially all of the sacrificial material may well have been removed using a suitable etch. A thermal barrier layer, e.g. a layer of SiO_2 having a low thermal diffusivity may be provided below the first layer in the gap to improve the downward flow of heat away from the first layer.

15

Of course, the device does not need to comprise a microbridge. It may, for example, comprise an alternate form of infrared sensing device. It may be a thin film piezoelectric actuator or a ferroelectric random access memory (FeRAM) or a dynamic random access memory (DRAM).

20

Most preferably the thickness of the first layer of ferroelectric material is greater than 2000\AA , or greater than 5000\AA , or up to $1\mu\text{m}$. Substantially all of the material throughout the thickness of the layer may exist in the perovskite phase which is annealed using the extended laser pulse.

25

In accordance with yet a further aspect, the invention provides a method of preferentially heating a first layer of material to a first temperature without heating a second layer of a material provided below said first layer to said first temperature by illuminating the first layer with a
30 temporally extended pulse of radiation from a laser source.

By temporally extending a pulse, the surface temperature of the first layer when illuminated with sufficient pulse energy to heat the whole layer up to or above the first temperature is lower than for a corresponding un-
5 extended pulse where the energy is supplied in a shorter period of time.

Of course, in an alternative the first layer may be heated to such an extent that the uppermost surface layer exceeds its melting point or is otherwise damaged. After annealing, this damaged (unwanted) layer could be milled
10 away or otherwise removed.

The first layer may comprise a material which is capable of existing in a ferroelectric state. The second layer may comprise a silicon base upon which an integrated circuit is formed. It is generally accepted that such
15 circuits will be damaged if heated in excess of 450°C, whilst most ferroelectric materials need to be heated in excess of 450°C to produce a high grade ferroelectric material. This can be achieved using the method of the present invention for layers of ferroelectric material up to at least 1µm in thickness.

20

Preferably, the pulse width is selected so that it is sufficiently long to ensure that the heat at the surface of the first layer diffuses away at a rate that keeps the surface temperature below melting, yet sufficiently long that the surface temperature of the second layer does not exceed the first
25 temperature. This will depend on the properties of the first layer and the wavelength of the pulse.

In accordance with a still further aspect, the invention provides a method of heat treating a treatment layer of an article comprising said treatment
30 layer and one or more further layers, the method comprising the steps of

illuminating the article with a laser pulse which is temporally extended by a temporal extender, the temporal width and fluence of the pulse being selected so that the treatment layer is raised to a treatment temperature T whilst one or more of the further layers are kept substantially below the treatment temperature T.

Preferably the treatment layer extends from a surface of the article downwards with one or more further layers below the treatment layer.

Alternatively, the treatment layer may be provided between one or more other layers.

The laser pulse may be temporally extended by partial reflection of a laser beam.

15

The heat treatment may comprise an annealing process. This may be adapted to convert the state of some or all of the material of the treated layer from its untreated state to a different treated state. An example is conversion of a ferroelectric material from a non-perovskite to a perovskite state, or from low grade perovskite to higher grade perovskite. Other treatments include heating to relieve locked in stresses within the first layer, or simply, to cause chemical change in the material of the layer or some other physical change of state.

In accordance with a still further aspect, the invention provides apparatus adapted to heat treat a treatment layer of an article comprising a treatment layer and one or more further layers, comprising a laser adapted to produce a laser pulse, a temporal extender adapted to extend the temporal width of the laser pulse, and means for guiding the temporally extended pulse onto the article, whereby the laser pulse is adapted to raise the

temperature of that treatment layer above a treatment temperature T whilst one or more of the further layers are kept substantially below the treatment temperature.

5 Looked at one way, an object of the invention in at least one arrangement is to provide a more uniform heating of the material in the first layer than can be achieved using standard commercially available laser devices. Alternatively, it may be considered as a technique and apparatus for reducing the surface temperature at the first layer by providing the
10 required heat energy at a slower rate using an extended pulse. In another aspect, the invention ensures that heat is kept away from unwanted areas of the article by providing a suitable duration extended pulse which provides more controlled and accurate heating of the layer of material.

15 There will now be described, by way of example only, one embodiment of the present invention with reference to the accompanying drawings of which:

20 **Figure 1** is a representation of an integrated uncooled IR detector having a ferroelectric layer that is annealed in accordance with the present invention;

Figure 2 is a plot of the measured temporal pulse shape for a prior art Lambda Physik LPX210i excimer laser;

25 **Figure 3** illustrates a set of predicted prior art temperature profiles through 1 micron of PST due to exposure to a non-extended laser pulse of width 25nm and a fluence of $0.1\text{J}/\text{cm}^2$;

30 **Figure 4** illustrates the predicted prior art temperature profiles

through the depth of the PST layer stack during and after exposure to a non-extended laser pulse with fluence $0.1\text{J}/\text{cm}^2$;

5 **Figure 5** illustrates the measured temporal pulse shape for a x 10 pulse-extension action with a 35ns interpulse delay using an excimer laser as in accordance with the present invention;

10 **Figure 6** shows predicted temperature profiles for a 1 micron layer of PST when exposed to an extended laser pulse with fluence $0.2\text{J}/\text{cm}^2$;

15 **Figure 7** shows predicted temperature profiles through the depth of the PST layer stack during and after exposure to an extended laser pulse with fluence $0.2\text{J}/\text{cm}^2$;

20 **Figure 8** is an XRD θ - 2θ scan of as deposited, unannealed, layer of sol-gel PZT;

25 **Figure 9** is an XRD θ - 2θ scan of pulse-extended laser annealed sol-gel PZT; and

30 **Figure 10** is a cross-section illustrating a typical microbridge device annealed in accordance with the invention; and

35 **Figure 11** illustrates an apparatus of one embodiment of the invention.

In order to quantify the improvements that are attainable using a method and apparatus in accordance with the present invention a model of the temperature profiles throughout a typical infra-red sensing device was

developed and experimental data was obtained using both a prior art single pulse laser and a pulse-extended laser in accordance with the invention.

- 5 The diffusion equation for heating of an arbitrary material using laser radiation has been solved. Assuming the layer stack and the irradiating laser beam to be uniform in the x-y plane, the later due to the use of a beam homogeniser, then the equation can be expressed in a uni-dimensional form as:

10

$$\frac{\partial T}{\partial t} = \frac{\alpha}{\rho c_p} I(z, t) + \sigma \epsilon (T^4 - T_a^4) + \frac{1}{\rho c_p} \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right)$$

- where $I(z, t)$ is the power density of the laser light at a depth z and at a time t , T is the temperature in the absorbing medium, T_a is the ambient
 15 temperature of the annealing chamber and ϵ, ρ, C_p, k and α are the emissivity, density, specific heat, thermal conductivity and absorption coefficient respectively. By inputting the thermal properties of a ferroelectric material such as PST and the temporal form of the laser pulse applied to the material, the temperature distribution throughout the
 20 material can be estimated. It should, however, be noted that the effect of latent heat due to the formation of the perovskite phase was not taken into account, but this does not effect the invention.

- The structure of a typical sensor is shown in cross section in Figure 10
 25 and in plan in Figure 1 of the accompanying drawings (and in Table 1 on page 3)

The sensor comprises a microbridge 10 as shown in Figure 1 which has a main detector area 12 which forms a single pixel in an array of pixels in

an imaging device. The main detector area 12 comprises a bridge 14 of sensing material that is responsive to incident radiation, typically a ferroelectric material such as Lead Scandium Tantalate. The microbridge area is typically 50 microns by 50 microns. The leg width is around 5
5 microns, and the length of the leg around 30 microns. The sensing sensing material is provided with electrically conducting coatings on both the lower and upper faces. The coating on the upper face is patterned to be only on the upper bridge body area. The coating on the lower face is patterned in the same shape as the sensing material, and thus is continuous
10 down the microbridge legs. An electrical discontinuity (not shown) in the lower coating separates the bridge 14 into two areas. A substrate or base layer (not shown) of silicon is provided, and the bridge 14 is supported away from the silicon base layer by a pair of legs 18 which slope down to contact the main detector area 12 at diagonally-opposed corners 20 and
15 22. Feet 24 and 26 of the legs contact the silicon base layer.

Figure 10 shows a cross-section view of the microbridge in Figure 2 taken so as to pass through the two feet of the microbridge (not to scale). In the arrangement of Figure 10, there is a silicon base layer or substrate A
20 which has a depth of, typically, 300 to 500 microns, a silicon dioxide insulating layer B extending above the silicon layer with a depth of about 0.5 microns, a space G (filled with sacrificial material during the manufacture of the device) with an average depth of 1 to 2 microns, a titanium layer and a platinum layer D (titanium of the order of 100\AA ,
25 platinum layer of the order of $1,000\text{\AA}$), a ferroelectric layer E, in this example of Lead Scandium Tantalate having a depth/thickness of about 1 micron, and a titanium layer F having a depth of about 100 to 200\AA .

The upper and lower surfaces of the ferroelectric material have metallic
30 coatings. The metal coating on the lower surface comprises a platinum

layer overlaying in titanium layer. The metal coating on the upper surface comprises a titanium layer. The distance between the conducting layers D and F of Figure 2, referenced H, when combined with the refractive index of the sensing material, results in an optical path equal to
5 one quarter of the wavelength of the radiation to which the microbridge is to be sensitive. Thus, the microbridge is tuned for absorption to a particular wavelength by the thickness of the thermally sensitive layer. For 10 micron wavelength radiation this translates to around 1 micron physical thickness for most ferroelectric ceramic materials, and preferably
10 for lead scandium tantalate. For optimum absorption, the titanium coating on the upper surface has a sheet resistance matched to free-space i.e. 377ohms per square, and the platinum coating on the lower surface has a high infra-red reflectance i.e. is over 100 nanometers thickness. The lower coating has a discontinuity, I, (to give, effectively, two parallel-
15 plate capacitor plates connected back-to-back in series). This allows the lower coating to be used to give two contacts to the sensing material and allows the upper coating to be electrically floating.

Conductive metal interconnect tracks, C, are provided on the silicon base
20 layer, to connect the signals from the microbridge to the read-out electrodes. The silicon base layer is coated with an insulating layer, B, in this case silicon dioxide, to electrically insulate the interconnect tracks. The two halves of the lower coating on the sensing material are connected each to a separate interconnected track on the silicon base layer. In an
25 imaging device where readout electronics are in the base silicon layer, then the interconnect tracks will be patterned with the read-out electronics i.e. under the silicon dioxide or other similar passivation layer, B, and the contacts to the microbridge will be through a via in the passivation layer.

30 Shown in Figures 3 and 4 are the temperature distributions throughout the

layers of the device of Figure 10 due to a 25cm wide laser pulse from an excimer laser with a fluence of $0.1\text{J}/\text{cm}^2$. The temperature distribution was modelled in simulation by ten discrete $0.1\mu\text{m}$ thick layers, the mean temperatures of which are shown as a function of depth in Figure 4. The surface temperature is very high as well as the temperature gradient through the PST layer. Figure 4 shows the temperature distribution with distance from the irradiated surface. Again, high temperature gradients and excessive surface heating are apparent.

In order to solve the problem of the high surface temperature, an apparatus in accordance with an aspect of the invention has been proposed. This is illustrated in Figure 11. It comprises a commercial excimer laser 100 controlled by a computer 101 which produces a light pulse with a pulse duration at full width at half maximum (fwhm) of 25ns. The output of the laser 100 is passed through a variable attenuator 150 and a temporal extender 200 which effectively increases the pulse duration and hence the diffusion length. The extended laser pulse is then passed through an anamorphic telescope 210 and a beam homogeniser 220 to a vacuum chamber 300.

20

The vacuum chamber 300 incorporates a heating plate 301 upon which a wafer 302 containing an unprocessed sensor is placed behind a UV transparent window 303. The heat raises the ambient temperature of the wafer defining the sensor, and the pulsed laser beam anneals the PST layer into a layer in the perovskite phase. A vacuum pump 304 is provided for evacuating the chamber whilst an inlet 305 allows a process gas to be introduced to the chamber.

A measured temporal profile from the apparatus is shown in Figure 5. Ten sub-pulses can be seen corresponding to the main pulse extension

action and then decaying subsidiary pulses which correspond to imperfections in the system. The pulse extender has increased the pulse duration from a full width at half maximum of 25ns to one of 350ns.

- 5 Assuming the pulse to have a fluence of $0.1\text{J}/\text{cm}^2$ (as for the unextended pulse) the effect of the pulse on the layers is shown in Figure 6 for the mean layer temperatures and in Figure 7 for the temperature distribution with distance from the irradiated surface at various times. Again, a $1\mu\text{m}$ layer of PST modelled as ten $0.1\mu\text{m}$ layers was assumed.

10

The effect of the pulse extender is to effectively slow down the rate of energy delivered to the surface thereby giving the heat generated more time to diffuse away. The surface temperatures are correspondingly lower than for the non-extended pulse with lower thermal gradients, and hence
15 an average higher temperatures, within the whole of the PST layer. Clearly, the pulse length is still sufficiently short to prevent the temperature of the topmost surface of the silicon wafer - where the active circuitry resides - from rising more than a few degrees above the ambient temperature of the wafer as a whole.

20

Initial studies using apparatus based on the arrangement shown in Figure 11 with sol-gel deposited PZT have shown that the technique is capable of crystallising amorphous as-deposited material into the required ferroelectric perovskite phase without damaging the underlying ROIC.
25 Figure 8 shows an x-ray diffraction (XRD) θ - 2θ scan of the material as deposited. The reflections present which are visible in the Figure are due to the platinum underlining the PZT and an intermetallic which forms due to a reaction between the platinum in the substrate and the lead in the as-deposited PZT.

30

Figure 9 shows a similar XRD θ - 2θ scan of the pulse-extended excimer laser annealed material with 10^4 pulses at a fluence of $80\text{mJ}/\text{cm}^2$ with the substrate heated to an ambient temperature at 300°C in an oxygen filled chamber. Reflections from perovskite PZT can be clearly observed

5 showing that the material has been crystallised into the correct phase.

CLAIMS

1. A method of producing an integrated ferroelectric device comprising a first layer of material capable of existing in a ferroelectric
5 state and a second layer of material defining an integrated circuit, the method comprising the steps of:

producing a pulse of energy having a first temporal width;

10 extending the temporal width of said pulse by passing it through a temporal extender to produce a processed pulse having a greater temporal width; and

illuminating the first layer with said processed pulse to convert some or
15 all of the material in the first layer from a non-ferroelectric state into a phase capable of exhibiting ferroelectricity or otherwise improving the quality of the material of the first layer without exceeding the temperature budget of the integrated circuit of said second layer.

20 2. A method according to claim 1 which further comprises generating a number of such processed pulses and sequentially illuminating the device with said pulses.

3. A method according to claim 1 or claim 2 in which the material of
25 the first layer comprises a low grade deposited perovskite and the method improves the quality of the perovskite material.

4. A method according to claim 1 or claim 2 in which the first layer
comprises material deposited substantially in a non-perovskite phase and
30 the method converts some or all of the material into the perovskite phase.

5. A method according to any preceding claim in which the pulse of energy comprises a pulse of energy produced using a laser.
6. A method according to claim 5 in which the laser pulse is produced using an excimer laser.
7. A method according to claim 5 in which the pulse is produced using a CO₂ laser.
8. A method according to any one of claims 5 to 7 in which the pulse produced by the laser has a temporal length of substantially 10ns, or 20ns or perhaps substantially 25ns, or even beyond or any value within a range of values limited by one or more of the preceding values.
9. A method according to any preceding claim in which the temporal extender increases the temporal length of the pulse to produce a processed pulse with a temporal length of approximately 300ns, or between substantially 300ns and 400ns, or longer.
10. A method according to any preceding claim in which the processed pulse comprises more than one sub-pulse, each sub-pulse corresponding to a pulse action of the extender.
11. A method according to claim 10 in which each sub-pulse is produced by partial reflection of the unprocessed pulse within the temporal extender.
12. A method according to any preceding claim in which the processed pulse has a fluence and temporal width that is compatible with the properties of the material of the first layer such that the temperature

throughout the layer (or over a substantial depth of the first layer) exceeds a predetermined anneal temperature whilst the temperature of the second layer is within the temperature budget of the circuitry.

- 5 13. A method according to any preceding claim in which the first layer comprises a layer of PST (or other material) of thickness of substantially 0.1 μ m, or substantially 1 μ m, or substantially 0.8 μ m or substantially 1.2 μ m or any value therebetween.
- 10 14. A method according to any preceding claim in which the first layer comprises the top layer of the device.
- 15 15. A method according to any preceding claim in which two different sources of energy are produced, each source producing a respective pulse and at least one of said respective pulses being extended by a pulse extender to produce a processed pulse, and in which the first layer is illuminated by both pulses.
- 20 16. A method according to claim 15 in which the layer is illuminated by both pulses substantially simultaneously.
- 25 17. A method according to claim 15 or claim 16 in which the two sources of energy comprises two different lasers, each generating a pulse of a different wavelength.
18. A method according to claim 17 in which one source comprises a KrF excimer laser, whilst the other source comprises a carbon dioxide (CO₂) laser.
- 30 19. A method according to any one of claims 15 to 18 which further

comprises providing a metallic layer between the first layer and the second layer and illuminating the first layer with the two different processed pulses.

5 20. A method according to any preceding claim in which the fluence of the processed pulse is substantially 0.05 J/cm^2 , 0.1 J/cm^2 , 0.2 J/cm^2 or a higher value or a lower value.

21. A method according to any preceding claim in which the first layer
10 is illuminated with the processed pulse whilst the ambient temperature of the device is maintained higher than room temperature.

22. A method according to claim 21 in which an ambient temperature in the range 100°C - 450°C , or 200°C - 450°C , or any other range between
15 the limits 100°C and 500°C approximately is used.

23. An apparatus for producing an integrated ferroelectric device, said device comprising at least a first layer of material capable of existing in a perovskite phase and second layer of material defining an integrated
20 circuit, the apparatus comprising:

pulse generating means adapted to generate a pulse of energy having a first temporal width;

25 pulse extending means adapted to extend the temporal pulse width of said pulse to provide a processed pulse of greater temporal width;

and guide means adapted to guide said processed pulse of energy onto said first layer whereby some or all of the material in the first layer is
30 converted from a non-ferroelectric state into a ferroelectric state or to

otherwise improve the quality of the material of the first layer without exceeding the temperature budget of the integrated circuit of said second layer.

5 24. Apparatus according to claim 23 which further comprises depositing means for depositing said first layer of material above said second layer in which some or all of said first layer is in a non-perovskite phase.

10 25. Apparatus according to claim 23 or claim 24 in which the pulse generating means comprises a laser.

26. Apparatus according to claim 25 in which the laser has a wavelength in the ultraviolet spectrum.

15

27. Apparatus according to any one of claims 23 to 25 in which the depositing means is adapted to deposit a first layer of material above the second layer after one or more intermediate layers are deposited onto the second layer.

20

28. Apparatus according to claim 27 in which one of the intermediate layers comprises a sacrificial layer that is subsequently removed to leave a space between the first and second layers to form a microbridge.

25 29. Apparatus according to claim 28 in which removal means is provided for removing the sacrificial layer.

30. Apparatus according to any one of claims 23 to 28 in which the device comprises a thermal detector.

30

31. Apparatus according to any one of claims 23 to 30 in which an array of devices is provided and the processed pulse illuminates more than one or all of the devices in the array simultaneously.

5 32. Apparatus according to any one of claims 23 to 30 which further includes means for raising the ambient temperature of the integrated device during annealing.

10 33. Apparatus according to any one of claims 23 to 32 which further comprises means for evacuating the air from around the device during annealing.

15 34. Apparatus according to any one of claims 23 to 33 in which the pulse extender is adapted to increase the temporal pulse width of the first pulse by substantially two times or four times, or substantially ten times or more than ten times or any value therebetween.

20 35. Apparatus according to any one of claims 23 to 34 in which the pulse extender is adapted to produce a processed pulse that comprises a number of sub-pulses, each sub pulse corresponding to the first pulse.

25 36. Apparatus for producing an integrated ferroelectric device substantially as described herein with reference to the accompanying drawings.

37. An integrated ferroelectric device comprising at least a first layer of ferroelectric material and a second layer comprising an integrated circuit, in which said first layer is transformed into a perovskite phase using a pulse of energy from a laser that has been temporally extended.

38. A device according to claim 37 in which the first layer comprises a material selected from the class of material which can exist in a perovskite phase.

5 39. A device according to claim 37 or claim 38 in which the second layer comprises silicon and or silicon oxide to define the integrated circuit.

10 40. A device according to any one of claims 37 to 39 which comprises a microbridge.

41. A device according to any one of claims 37 to 40 in which the thickness of the first layer of ferroelectric material is greater than 2000Å.

15 42. A device substantially as described herein with reference to the accompanying drawings.

20 43. A method of preferentially heating a first layer of material to a first temperature without heating a second layer of a material provided below said first layer to said first temperature by illuminating the first layer with a temporally extended pulse of radiation from a laser source.

25 44. A method according to claim 43 in which the first layer is heated to such an extent that the uppermost surface layer exceeds its melting point or is otherwise damaged and after annealing the damaged layer is milled away or otherwise removed.

45. A method according to claim 43 or claim 44 in which the first layer comprises a material which is capable of existing in a ferroelectric state.

46. A method according to any one of claims 43 to 45 in which the second layer comprises a silicon base upon which an integrated circuit is formed.

5 47. A method according to any one of claims 43 to 46 in which the pulse width is selected so that it is sufficiently long to ensure that the heat at the surface of the first layer diffuses away at a rate that keeps the surface temperature below melting, yet sufficiently long that the surface temperature of the second layer does not exceed the first temperature.

10

48. A method of heat treating a treatment layer of an article comprising said treatment layer and one or more further layers, the method comprising the steps of illuminating the article with a laser pulse which is temporally extended by a temporal extender, the temporal width and
15 fluence of the pulse being selected so that the treatment layer is raised to a treatment temperature T whilst one or more of the further layers are kept substantially below the treatment temperature T.

49. A method according to claim 48 in which the treatment layer
20 extends from a surface of the article downwards with one or more further layers below the treatment layer.

50. A method according to claim 48 in which the treatment layer is provided between one or more other layers.

25

51. A method according to claim 48 or 49 or 50 in which the laser pulse is temporally extended by partial reflection of a laser beam.

52. A method according to any one of claims 48 to 51 in which the heat
30 treatment comprises an annealing process.

53. Apparatus adapted to heat treat a treatment layer of an article comprising a treatment layer and one or more further layers, comprising a laser adapted to produce a laser pulse, a temporal extender adapted to extend the temporal width of the laser pulse, and means for guiding the temporally extended pulse onto the article, whereby the laser pulse is adapted to raise the temperature of that treatment layer above a treatment temperature T whilst one or more of the further layers are kept substantially below the treatment temperature.

ABSTRACT
IMPROVEMENTS RELATING TO ANNEALING

5 A method and apparatus for annealing an integrated ferroelectric device is disclosed in which the device comprises a first layer of material capable of existing in a ferroelectric state and a second layer of material defining an integrated circuit below the first layer such as a microbridge thermal detector. The method comprises producing a pulse of energy, extending
10 the pulse temporally using a pulse extender and illuminating the first layer with the extended pulse. The duration and wavelength and fluence of the extended pulse are selected so that the material of the first layer is annealed into a ferroelectric state without exceeding the temperature budget of the integrated circuit. Application of the method in heating
15 other articles which comprise a layer to be heated and a temperature sensitive layer is also disclosed. By extending the temporal width of the pulse, energy is supplied at a rate which ensure a more even heating of the first layer without damaging the temperature sensitive layer over time.

20

To be accompanied, when published with Figure 5 of the drawings.

1/6

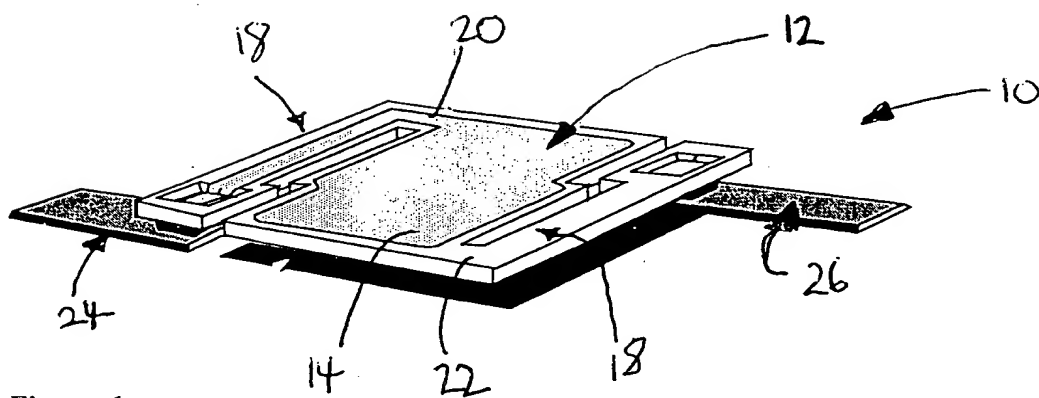


Figure 1.

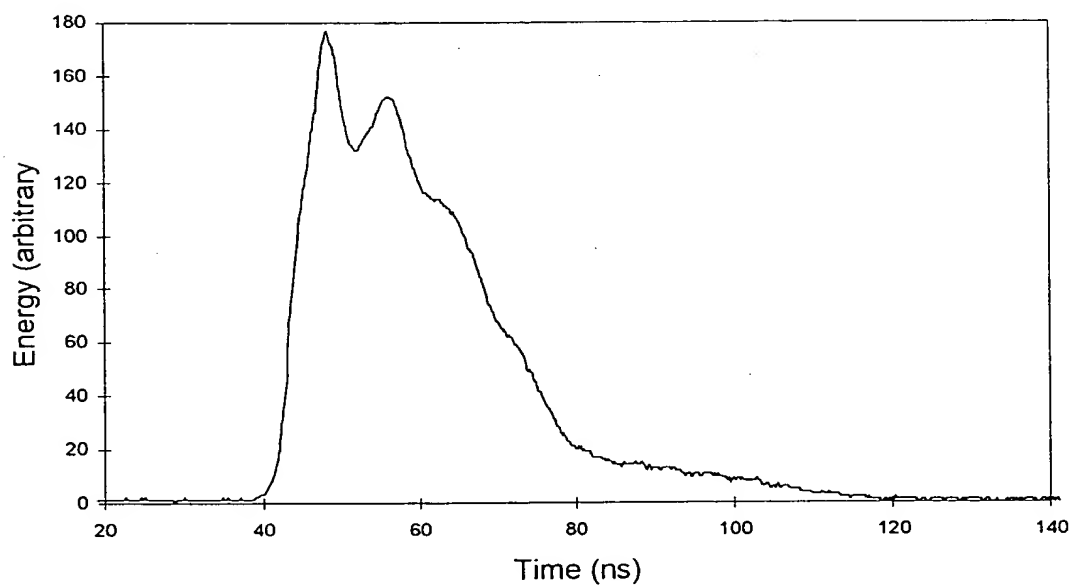


Figure 2.

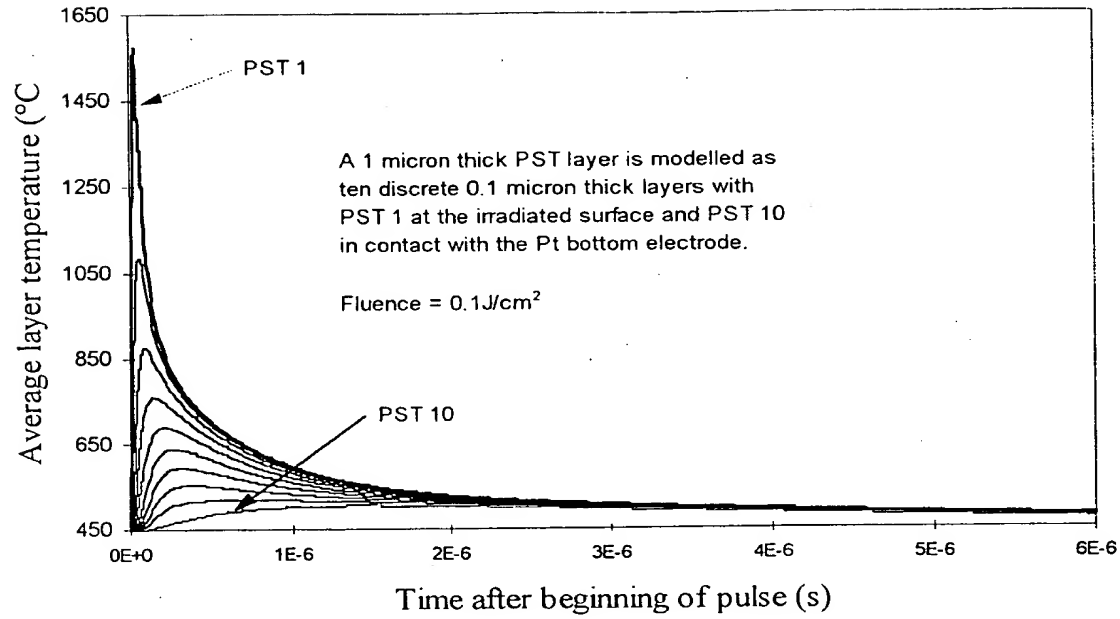


Figure 3.

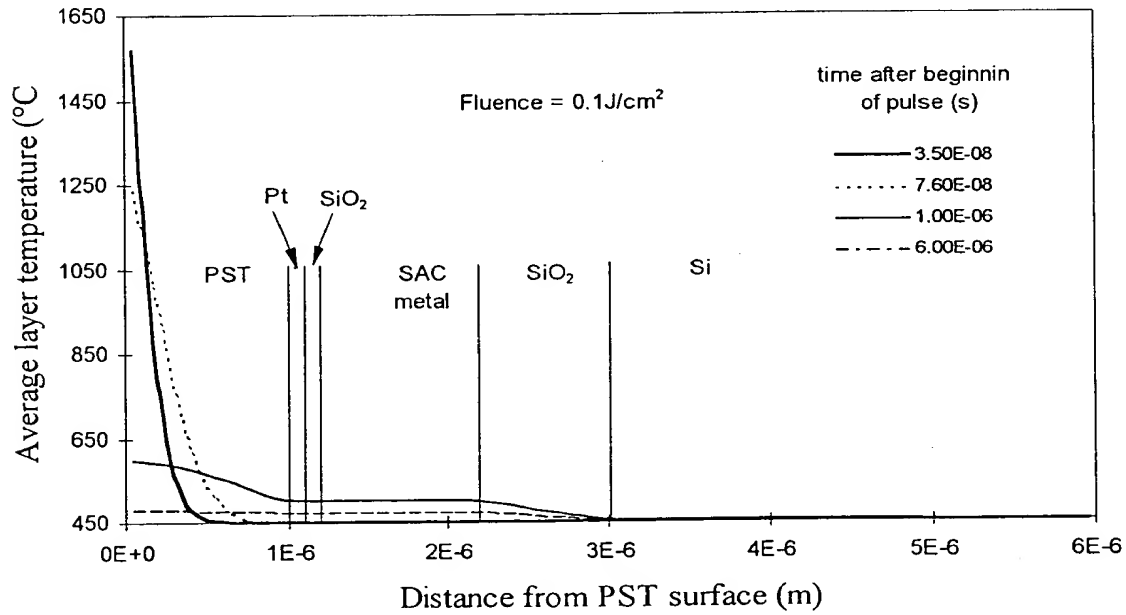


Figure 4.

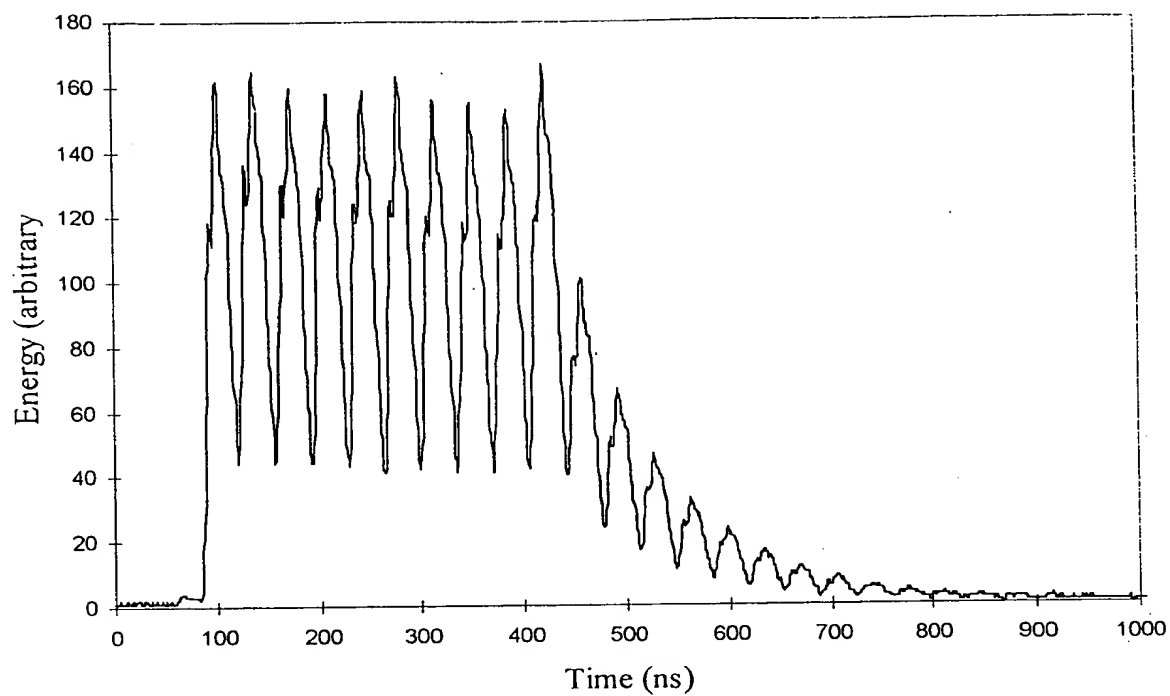


Figure 5.

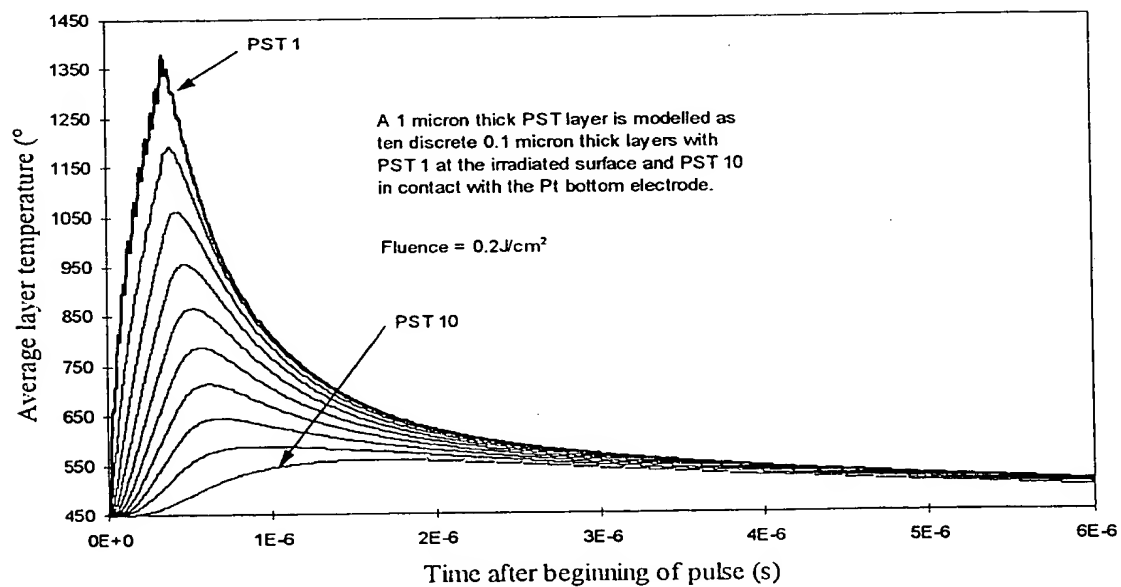


Figure 6.

4/16

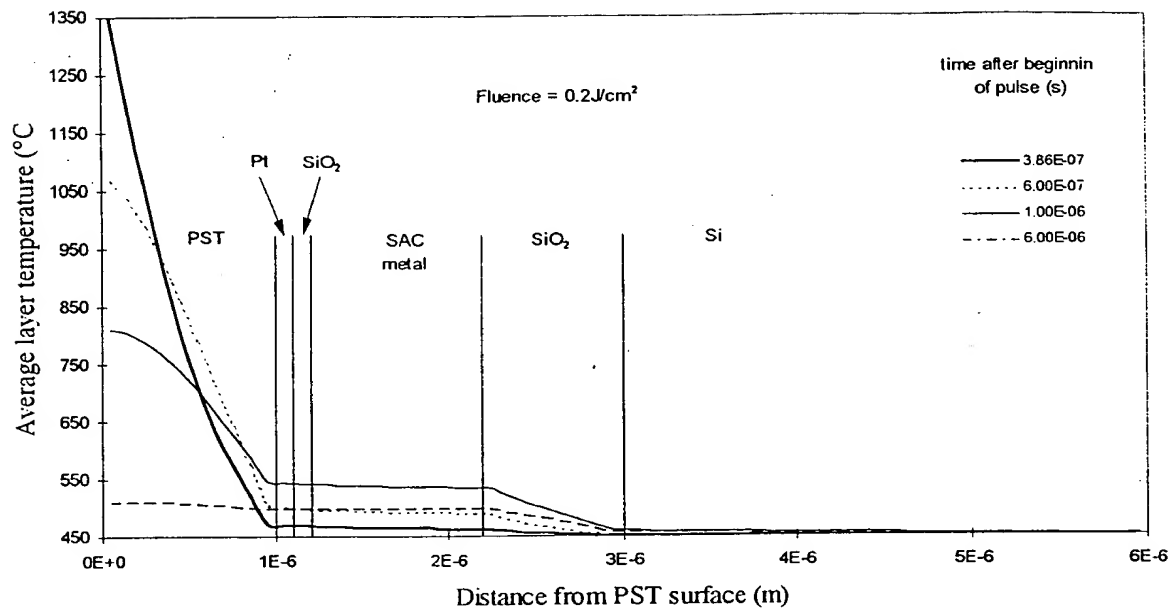


Figure 7.

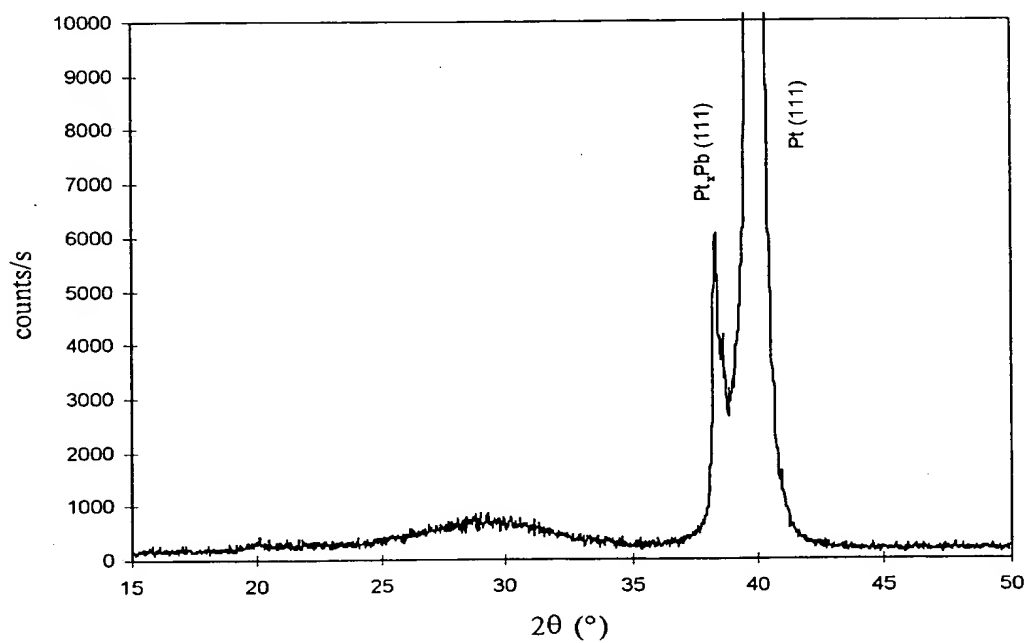


Figure 8.

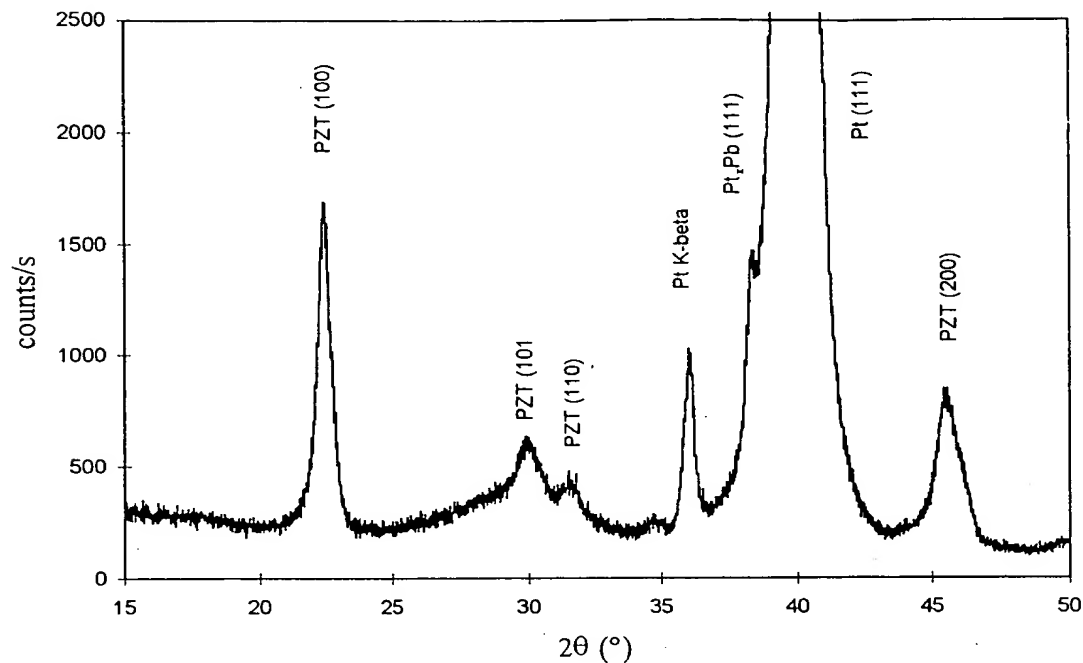


Figure 9.

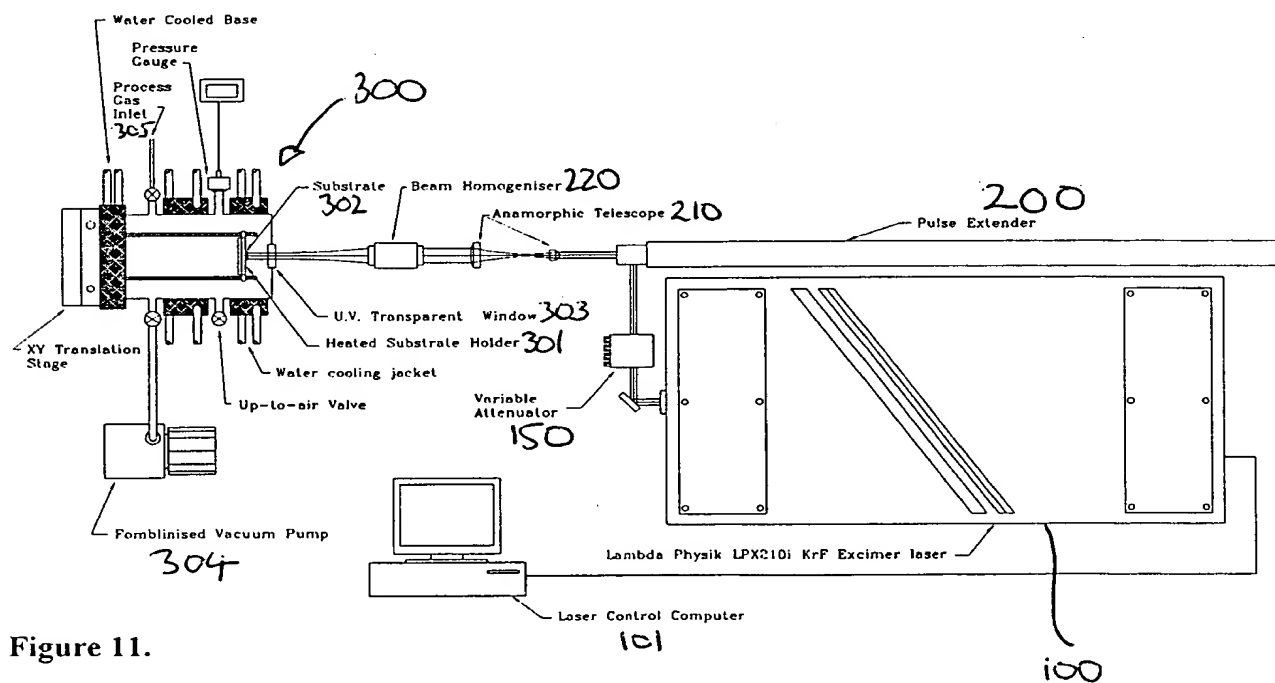


Figure 11.

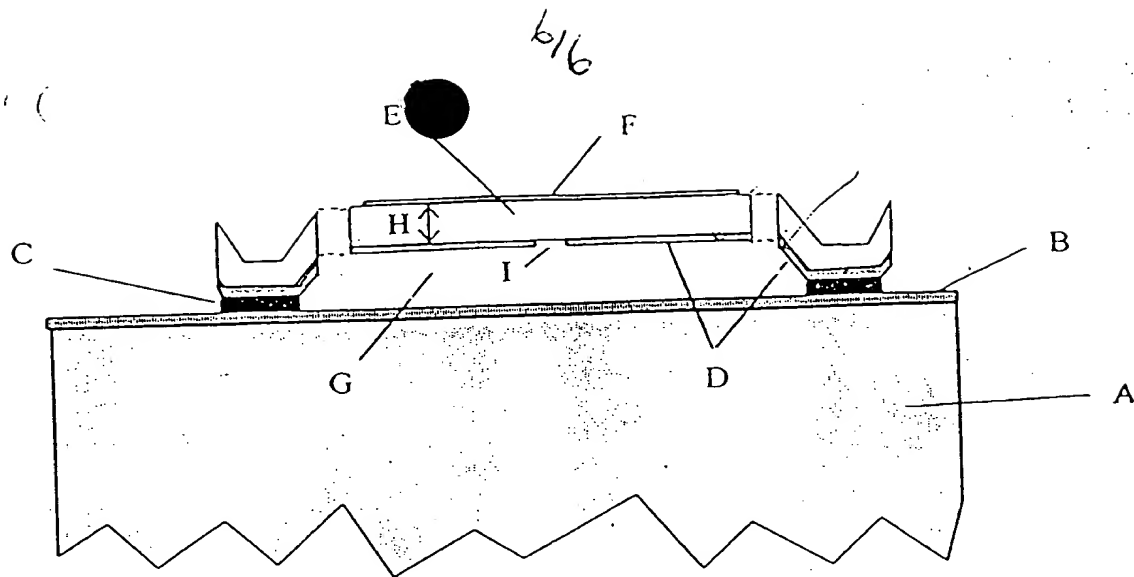


Fig 10

THIS PAGE BLANK (USPTO)